

THE INFRA-RED ABSORPTION SPECTRA
OF THE METHYL HALIDES

BY
WILLARD H. BENNETT

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY IN THE UNIVERSITY
OF MICHIGAN

THE INFRA-RED ABSORPTION SPECTRA
OF THE METHYL HALIDES

BY

WILLARD H BENNETT

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY IN THE UNIVERSITY
OF MICHIGAN



THE INFRA-RED ABSORPTION SPECTRA
OF THE METHYL HALIDES

BY WILLARD H. BENNETT AND CHARLES F. MEYER

ABSTRACT

The molecules are symmetrical tops having one low moment of inertia. Two types of bands are expected, one arising from vibration parallel to the axis of symmetry, $\parallel$ bands, and the other from vibration perpendicular to the axis of symmetry, $\perp$ bands; the appearance of each type is described. There are seven bands for each of the four compounds. The twenty-eight bands fall into seven series, *A* to *G* inclusive. Two of the four bands of series *A* lie beyond the range of observation. Series *A*, *C*, *E* and *F* are made up of bands of the $\parallel$ type, and series *B*, *D*, and *G*, of bands of the $\perp$ type. The series converge towards the known bands of methane with decrease in the atomic weight of the halogen in the halide. The envelopes of the bands of the $\parallel$ type demonstrate the existence of *P*, *Q*, and *R* branches. The doublet separations for the various bands of the same compound appear to be the same; the chloride may however present an exception to this rule. In passing from compound to compound, the doublet separations increase with decrease in the atomic weight of the halogen in the halide. The band of series *A* for methyl fluoride has been resolved, and it is revealed that the *P* and *R* branches consist of a single series of lines. Strong convergence in the spacing is present. The bands of the $\perp$ type have all been resolved. Every third line is more intense than the others. The spacing converges in series *B* toward lower frequencies, and in series *D* and *G* toward higher frequencies. The mean frequency intervals from band to band of the same compound are found to vary markedly. The explanation of this variation presents a theoretical problem of interest.

INTRODUCTION

RECENT improvements in the apparatus available for measuring infra-red absorption have made possible the detailed study of spectra of much greater complexity than could be observed only a few years ago. As a consequence, the spectra of polyatomic molecules containing more than one heavy atom have become subject to investigation. Theoretical considerations led to the belief that the vibration rotation spectra of the methyl halides, CH_3F , CH_3Cl , CH_3Br , CH_3I , in the gaseous state, offered a promising field for study.

Stereochemical evidence indicates that the molecules consist of a carbon atom lying within a tetrahedron, with the three hydrogen atoms and the halogen atom at the four corners. The supposed form of the molecule is represented in perspective in Fig. 1, the carbon atom being denoted by *C*, the three hydrogens by *H*, and the halogen which varies from compound to compound by *Z*. The carbon atom and the halogen determine an axis about which the hydrogen atoms are symmetrically placed. The center of gravity of the molecule probably lies between the carbon and the halogen. The principal axes of inertia lie along the lines marked *X*, *Y*, and *Z*, and the moments of inertia about these axes will be referred to as *A*, *B*, and *C* respectively. In the *XY*-plane the three axes which lie above the lines joining the hydrogen atoms

to the carbon are physically indistinguishable from each other, and consequently the moments of inertia about these axes will all be equal. From this it follows that the ellipsoid of inertia for this type of molecule degenerates into a spheroid and the moments of inertia about all axes in the XY -plane which pass through the Z -axis must be the same, therefore $A = B$. Moreover, if the distance of the halogen from the carbon were about the same as the distance of the hydrogens from the carbon then $A (=B)$ would be much greater than C , for the magnitude of the former would be determined principally by the masses of the relatively heavy carbon and halogen atoms, and the magnitude of the latter would be determined by the light hydrogen atoms.

The Z -axis is the only unique axis and the permanent electric moment of the molecule, which must in general be assumed to exist, consequently lies along this axis.¹ Considerations based upon an extension of the vibrations of the ammonia molecule² show that the normal modes of vibration of the methyl halides consist of two types. In the first type the electric moment, and hence the change of electric moment vibrates parallel to the axis of symmetry. A band arising from such a vibration will be referred to as a " $\parallel$ band," and the fine structure to be associated with it will be briefly discussed.

Simultaneous rotation of the molecule about the Z -axis would not influence the absorption because the axes of vibration and rotation are coincident. But rotation about an axis in the XY -plane would influence the absorption. Simultaneous changes in the vibration state and the rotation state about such an axis will give rise to a series of absorption lines which are in first approximation equally spaced at a frequency interval $\Delta\nu = h/4\pi^2 A$. These lines will form a P branch and an R branch which are schematically represented in Fig. 2a. In addition

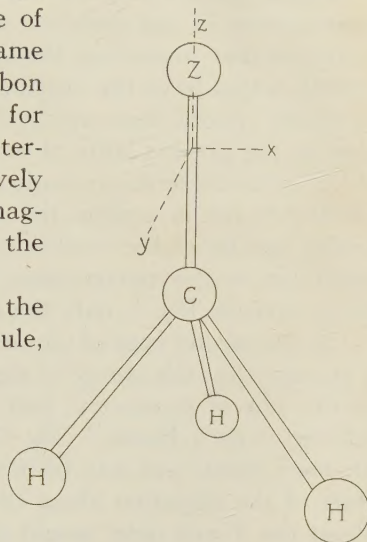


Fig. 1. Model of methyl halide molecule.

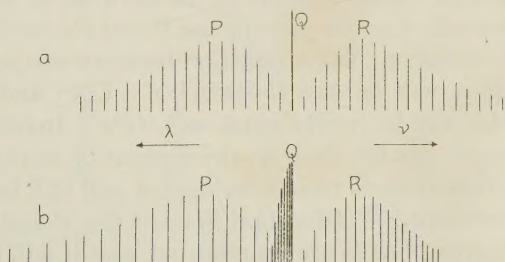


Fig. 2. Band of the $\parallel$ type.

¹ The remaining remarks of the introduction have as a basis the work of D. M. Dennison, *Phys. Rev.* **28**, 318 (1926); Reiche and Rademacher, *Zeits. f. Physik* **39**, 444 (1926); and Kronig and Rabi, *Phys. Rev.* **29**, 262 (1927), upon the rotation of molecules having the form of a symmetrical top.

² D. M. Dennison, *Phil. Mag.* **1**, 195 (1926).

tion there will be a Q branch of which the intensity will depend upon the ratio of the moments of inertia C/A . The smaller this ratio, the more nearly does the molecule resemble a diatomic one for which the ratio is zero and the Q branch is absent, as in the spectrum of hydrogen chloride.

Perturbations between the vibration and the rotation states will cause convergence in the positions of the lines in the P and R branches, these branches then presenting the appearance shown in Fig. 2b. Moreover the Q branch would have the modified appearance now indicated for it, consisting of closely spaced lines rapidly decreasing in intensity. The lines are so close that in the present state of technique there is no hope of separating them. When measurements are made upon a band of the type just described, and all conditions are favorable, the result is that of the upper curve of Fig. 5.³ Under less favorable conditions the lines of the P and R branches are not separated by the spectrometer, and the band presents the appearance of the lower curve of Fig. 5, only the *envelopes* of all three branches being obtained.

In the second type of vibration referred to above, the atoms move in such a manner that the *change* of electric moment is a vector lying perpendicular to the axis of symmetry, and bands arising from such a vibration will be referred to as " L bands." The fine structure is essentially more complex than for the $\parallel$ bands and may be described as follows: Simultaneous change in the state of the vibration along the X -axis and change in the state of rotation about the Y -axis only, would give rise to a band similar to the one already considered. But rotation about the Z -axis would no longer be without effect, since the Z -axis is now no longer parallel to the vibration of the electric moment, as in the $\parallel$ bands, but is perpendicular to it. Rotation about the Z -axis would cause the original band to be repeated at equal intervals to the right and to the left of the central position, with decreasing intensities. The separation between adjacent constituent bands would not be sufficient to separate them from each other entirely and they would overlap. In Fig. 3a such a group of constituent bands is shown, the individual members being placed higher or lower in the drawing so that they might be separately represented. Certain lines in the P and R branch near the center of each band will be missing. The separation between successive bands, expressed in frequency units will be $\Delta\nu = (h/4\pi^2)(1/C - 1/A)$ and since C is much smaller⁴ than A this will be nearly equal to $h/4\pi^2C$. Inasmuch as the moment of inertia C is much smaller than A , the separation between the bands, while insufficient to prevent them from overlapping will still be much greater than the separation between the individual lines of the P and R branches. In Fig. 3b the overlapping bands are represented, and it will be seen that what one may hope to find is a series of Q branches, well separated, and about equally spaced. Between them will lie numerous closely packed lines in apparently confused

³ The two faint lines appearing on the left slope of the Q branch are *not* lines of the Q branch, but are lines of the P branch which are superposed on the envelope of the Q branch.

⁴ It should perhaps be emphasized that $C \ll A$ is not a general property of the symmetrical top molecule, but it happens to characterize the methyl halide group.

arrangement, which one could not hope to separate but they will form a background of absorption. The appearance of a region of absorption arising from vibrations of the electric moment perpendicular to the axis of figure of the molecule will then be that represented schematically in Fig. 3b, or as actually observed it may be seen in Fig. 6. The region as a whole will be spoken of as

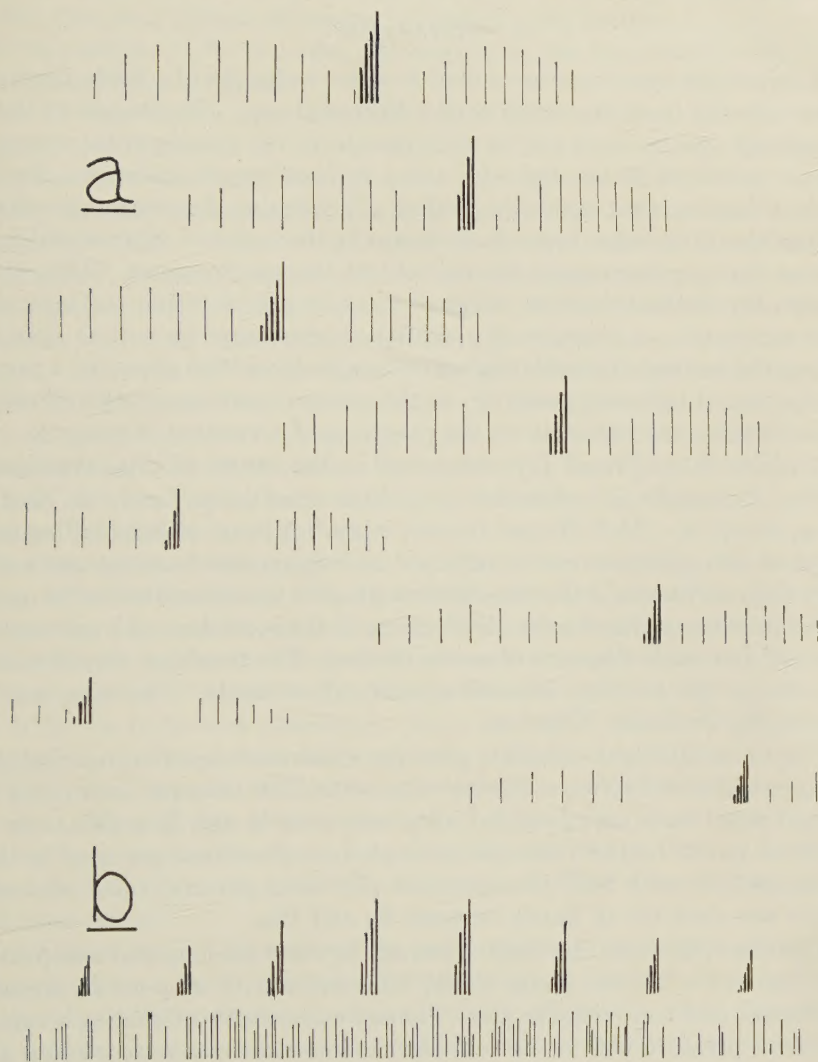


Fig. 3. Band of the $\perp$ type.

a $\perp$ band, and it will be noted that it consists of a single series of maxima which is most intense at the center of the band, being distinguished in this from bands of the $\parallel$ type which consist of three branches as already explained.

In order that the maxima (succession of Q branches) should be well separated, the moment of inertia C must be small. The supposed smallness of

this moment of inertia in the methyl halides was an important factor in determining the choice of this group of molecules for investigation. An equally important factor was that because of the symmetry of position of the hydrogen atoms the ellipsoid of inertia degenerates into a spheroid and consequently the molecules belong to the type known as a symmetrical top.

APPARATUS

A fore-prism spectrometer is used to select radiation of a fairly large range of wave-length from the emission of a Nernst glower. This is passed through the gas cell and focussed on the entrance slit of the grating spectrometer. A concave mirror of 20 cm diameter and 1 m focal length collimates the beam which is then incident upon the grating. The grating disperses the radiation, sending the first order beam back towards the concave mirror which now focusses the spectrum upon the exit slit of the spectrometer. This slit lets through the ultimate narrow range of wave-length of which the intensity is to be measured. A diagram of a similar spectrometer as well as details regarding the method of calculating wave-lengths have been given by a previous investigator of infra-red spectra.⁵ In the present instrument a small concave mirror focusses the radiation on the junctions of a vacuum thermopile. Two thermopiles of the Pfund⁶ type were used in the course of this investigation.

The thermopile is connected to a high sensitivity Leeds & Northrup galvanometer in a Moll-Burger thermo-relay.⁷ A beam of light falling on the mirror of this galvanometer is reflected and thereupon focussed midway between the junctions of a thermo-element which is in turn connected to another high sensitivity galvanometer. Deflections of the secondary galvanometer are observed at a scale distance of seven meters. The resulting amplification is from one to two hundred depending upon adjustments. The relay was constructed by Professor Firestone.

The three Michigan echelette gratings which were used, were ruled under the supervision of Professor Barker. One with 7200 lines per inch (2834 lines per cm) ruled on a copper-nickel alloy was used in the 3μ region, one with 2880 lines per inch (1134 lines per cm) ruled on aluminum was used in the 7μ region, and one with 1440 lines per inch (567 lines per cm) ruled on a solder surface was used for all bands between 8μ and 15μ .

The absorption cell was built of brass. It was 6 cm long and was provided with rock-salt windows 5 mm thick. Side tubes with stop-cocks served for introducing and removing the gas. The cell was capable of holding a vacuum; the rise of pressure within the cell, after it had been evacuated, being about 0.1 mm in the course of two days. A pump, an ordinary manometer and a McLeod gauge served for controlling and measuring the pressure of gas used in each run. Pressures were known to within 1 mm for all runs.

⁵ W. W. Sleator, *Astrophys. J.* **48**, 125 (1918).

⁶ A. H. Pfund, *Phys. Zeits.* **13**, 870 (1912).

⁷ W. J. H. Moll, and H. C. Burger, *Phil. Mag.* **50**, 624 (1925).

SOURCES OF MATERIAL

Methyl chloride was obtained from the Dow Chemical Company in cylinders. An analysis furnished by the manufacturers indicated a sufficient degree of purity.

Methyl bromide (C.P.) was at first obtained from Kahlbaum, and later from the Eastman Kodak Company, in sealed glass bottles.

Methyl iodide (C.P.) was also obtained from the Eastman Kodak Company, in sealed glass bottles.

Methyl fluoride was not available from any chemical manufacturing company, and therefore it was necessary to find an efficient laboratory method for its preparation in a sufficiently pure state for spectroscopic work. The best method of preparation found was as follows: Potassium fluoride, hydrate, $\text{KF} \cdot 2\text{H}_2\text{O}$, (Baker), was heated until the water of crystallization had boiled off, leaving a white mass of anhydrous potassium fluoride, KF . This was pulverized. Potassium methyl sulfate, crystalline, KCH_3SO_4 (Eastman), was pulverized, and mixed with the pulverized potassium fluoride in the ratio—two parts KF to five parts KCH_3SO_4 . The mixture was heated to $140\text{--}200^\circ\text{C}$. The gas evolved was passed: (1) through concentrated sulfuric acid in a spiral wash bottle with a gas path of about 65 cm, (2) through a concentrated solution of potassium hydroxide, (3) through a drying tube of soda lime and two drying tubes of calcium chloride (fused), and, (4) into a condenser submerged in liquid air.

The impurities which might be expected from reactions occurring in heating $\text{KF} + \text{KCH}_3\text{SO}_4$ are CO_2 , H_2O , $(\text{CH}_3)_2\text{O}$, C_2H_4 and SO_2 . The KOH takes out the CO_2 and SO_2 quantitatively while the CaCl_2 removes the H_2O . A spectroscopic test by the method of infra-red absorption was made for the possible impurities $(\text{CH}_3)_2\text{O}$ and C_2H_4 . In this, the spectral region extending from 10.5μ to 11.5μ was examined. Here both $(\text{CH}_3)_2\text{O}$ and C_2H_4 absorb strongly, but methyl fluoride is transparent. When the supposed impurities were introduced into the cell at *low* pressures there was marked absorption. But when the cell was filled with methyl fluoride as above prepared, to *atmospheric* pressure, there was no measureable absorption. Hence it may be concluded that the methyl fluoride is practically free from the impurities which were feared.

Precautions were taken to secure pure materials, and furthermore, the spectra which have been obtained constitute evidence, through their regularity, that the absorption curves are not appreciably affected by impurities which might supposedly have been present.³ This evidence becomes especially convincing when the spectra of the four compounds are considered in relation to each other.

METHOD OF OBSERVATION

The grating is set at equal intervals throughout the spectral region under examination. At each setting of the grating deflections are taken both with

³ One of the bands of methyl iodide presents a possible exception to this statement. It is the band of Series E, Fig. 8.

the cell in the beam and out of it, the cell being mounted so that it can be raised or lowered by a control lever. Because of reflection and slight absorption by the rock-salt windows of the cell a certain apparent absorption exists with the cell empty. For each band a run was made both with the cell containing gas at a known pressure, and also with the cell rinsed with air and then evacuated to less than 1 mm pressure. The percent transmission of the cell filled with gas, divided by the percent transmission of the evacuated cell gives the true percent of absorption of the gas. From the data thus obtained, curves are plotted with grating settings as abscissas and percentages of absorption as ordinates.

Preliminary explorations were made of the spectra of methyl fluoride and methyl chloride with a small prism spectrometer, and the results were plotted together with the observations made by W. W. Coblentz⁹ on methyl iodide. The bands for these three substances were found to fall into regular series and it was assumed that the position of the bands of methyl bromide could be located by interpolation. Later observations with the grating spectrometer proved this assumption to be correct.

Further preliminary observations were made of all bands with the grating spectrometer, using large slit widths, and with large intervals between successive settings of the grating. This was done both to find the locations of the bands more accurately than was possible with the prism spectrometer, and also to find the amount of gas which it was necessary to have in the beam to give the best definition of the lines. Definition is best when the maximum of absorption of a band is at about fifty percent.

It is necessary to determine by trial the width of slit which is most favorable for each band. These trials were often very time consuming. As the slit width is cut down, the galvanometer deflection decreases as the square of the slit width, and the zero unsteadiness becomes a large, and intolerable percent of the total deflection. On the other hand, with too great a slit width, the fine structure of the bands becomes partially or totally obliterated. The errors of observation can be somewhat reduced by taking several deflections, but taking more than three or four is of doubtful value.

The final observations on most of the bands had to be taken between midnight and morning, since the galvanometer was too unsteady at other times. It was found necessary moreover to have the spectrometer in readiness for about an hour before beginning observations in order to allow conditions to become steady.

The spectrometer constants had been carefully determined for each of the three gratings used in another investigation which ran concurrently with this one,¹⁰ and these constants were used in computing frequencies.

GENERAL RESULTS

Seven distinct series of bands were found for this series of compounds. Figure 4 shows the locations of the bands, and the seven series are indicated

⁹ W. W. Coblentz, Publications of the Carnegie Institution of Washington, **35**, (1905).

¹⁰ A. Levin and C. F. Meyer, J.O.S.A. and R.S.I. **16**, 137 (1928).

by the letters *A* to *G* inclusive. The full vertical lines, series *A*, *C*, *E*, and *F*, represent $\parallel$ bands, and the dotted vertical lines, series *B*, *D*, and *G*, represent $\perp$ bands. The lengths of the lines are roughly proportional to the intensities of the bands, and the broken lines connect the bands of each series. The two bands of methane observed by Cooley¹¹ are shown at the top of the figure.

Only the first two members of series *A* could be observed. The two remaining members presumably lie at wave-lengths too great to be reached on account of the increasing opacity of rock-salt and the absorption due to the carbon dioxide of the atmosphere. Series *B*, 8.5μ to 11.3μ was completely observed. The two series *A* and *B* appear to converge toward the 7.7μ band of methane.

Two more series of bands, *C* and *D*, lie between 6.6μ and 8.0μ . When series *C*, which is of the $\parallel$ type is extrapolated to include a band for methane, this band will lie between 2μ and 6μ . The location of the analogous band of methane cannot be more definitely stated until the nature of the vibration

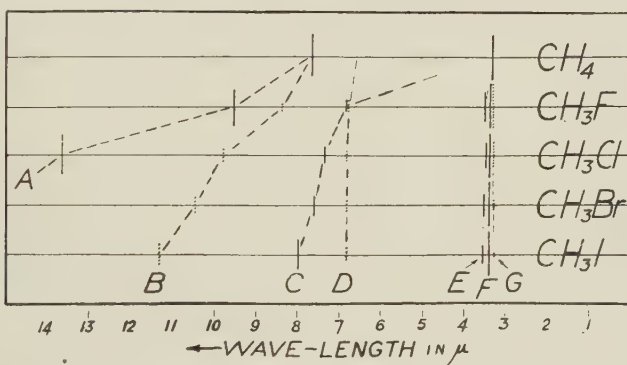


Fig. 4. Location of the bands of methane and the methyl halides.

causing this series of bands has been determined. The intensities of the bands of this series decrease toward methane and it is likely that the band of methane in this series is weak or entirely inactive.

Extrapolation of the wave-lengths of the bands of series *D*, which are of the $\perp$ type, toward a wave-length for methane indicates a band at about 6.6μ . The intensities decrease in this series, also toward methane. Dennison¹² predicted that an optically inactive band for methane should lie at 6.58μ . In series *C*, as in series *B*, the frequency intervals between the bands for the three heavier halides are nearly equal while that from the chloride to the fluoride is somewhat greater.

The region between 3.2μ and 3.6μ contains three series of bands, *E*, *F*, *G*, which converge toward the 3.31μ band of methane observed by Cooley. The central series, *F*, is of the $\parallel$ type and is the strongest of the three, remaining about equally strong and at nearly the same frequency throughout the series. On each side of this series is another series of bands, series *E* being of the $\parallel$

¹¹ J. P. Cooley, *Astrophys. Journ.* **62**, 73 (1925).

¹² D. M. Dennison, *Astrophys. Journ.* **62**, 84 (1925).

type and series *G* of the $\perp$ type. The intensities in these two series increase toward methane.

INDIVIDUAL SERIES

Series A, || type. The 9.55μ band for CH_3F is shown in Fig. 5 and the frequencies of the lines, as observed, are given in Table I. In the figure, the full line passes through all the points found experimentally while the dotted lines show slight idealizations which are thought to be well justified. This

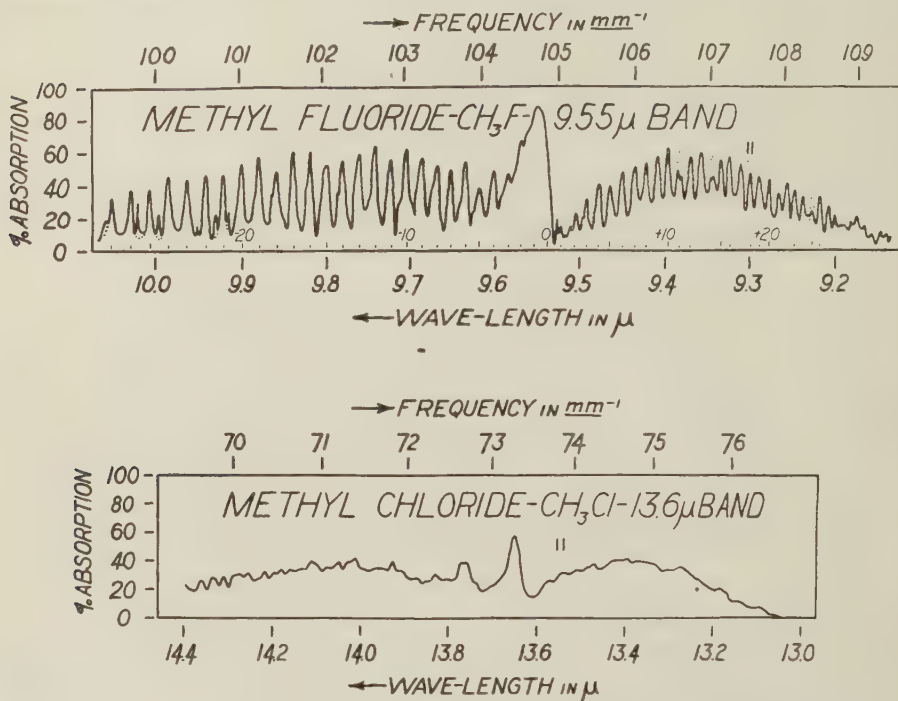


Fig. 5. The bands of series *A* which are accessible to measurement.

TABLE I. The band of methyl fluoride, Series *A*, || type.

Line No.	Observed Frequencies	Line No.	Observed Frequencies	Line No.	Observed Frequencies	Line No.	Observed Frequencies
-27	994.79 cm^{-1}	-13	1024.63 cm^{-1}	+ 1	—	+15	1071.21 cm^{-1}
-26	997.04	-12	1026.58	+ 2	1052.24 cm^{-1}	+16	1072.40
-25	999.28	-11	1028.56	+ 3	1053.57	+17	1073.97
-24	1001.50	-10	1030.60	+ 4	1055.15	+18	1075.21
-23	1003.73	- 9	1032.41	+ 5	1056.60	+19	1076.42
-22	1005.95	- 8	1034.40	+ 6	1058.21	+20	1077.90
-21	1008.03	- 7	1036.13	+ 7	1059.88	+21	1079.10
-20	1010.21	- 6	1038.00	+ 8	1061.31	+22	1080.24
-19	1012.24	- 5	1039.83	+ 9	1062.79	+23	1081.25
-18	1014.50	- 4	1041.58	+10	1064.18	+24	1082.50
-17	1016.55	- 3	1043.50	+11	1065.70	+25	1083.70
-16	1018.59	- 2	1045.02	+12	1067.19	+26	1084.81
-15	1020.62	- 1	—	+13	1068.59	+27	1086.04
-14	1022.60	0	(1048.52)	+14	1069.96	+28	1086.91

band was measured with the fluoride at a pressure of 4.0 cm. A scale is included in the figure for numbering the lines, the scale being so chosen that the number of a line is also the value of the quantum number m of the initial state in the transition which gives rise to the line. The slit width used covered a spectral range of 40A, and readings were taken at intervals of 25A.

The observed frequencies of the lines can be expressed as a quadratic function of the line number. With the frequency expressed in waves per centimeter the equation found is:

$$\nu = 1048.52 + 1.688m - 0.01125m^2$$

The differences between the observed and calculated values do not show systematic trend. If it were possible to observe the frequencies much more accurately it would probably be necessary to introduce a cubic term, but this could hardly be greater than 1×10^{-5} .

From the simple theory it was predicted that the lines should be linearly spaced, and the presence of a term of higher order implies a perturbation between the vibrational and rotational motion. Perturbation also gives varying values for the frequencies of the lines in the Q branch corresponding to the various values of the rotational quantum number, giving a Q branch which extends away from the fundamental frequency quite considerably. It is seen in the band for CH_3F that the Q branch rises steeply to a maximum value and then slopes off less steeply toward the P branch. This indicates a relatively large frequency interval between the successive unresolved lines of the Q branch.

The 13.6μ band of CH_3Cl is also shown in Fig. 5. The power of the spectrometer, although decidedly greater than that of spectrometers used heretofore, was not sufficient to define the lines of this band. Using the same slit width and taking readings at the same interval as for the 9.55μ band of CH_3F , it was found that the deflections were too small to be dependable, the available energy being smaller in this region. Using a slit-width of 60A and taking a large number of readings at each setting of the circle, it was found that a suggestion of the fine structure could be obtained but the definition was not sufficient to make a complete measurement of the band in this manner worth while. The envelope shown in the figure was measured with the gas in the cell at a pressure of 4.0 cm and using a slit width of 160A. It is to be noted in this band, as in the previous one, that the P branch extends over a greater range of frequency than the R branch, indicating that there is a large perturbation between vibrational and rotational motion also in the case of this compound.

The bands of series A for CH_3Br and CH_3I are not accessible to measurement, as has already been mentioned.

The frequencies for the maxima of the envelopes of the branches for the two bands of this series which were measured are given at the head of Table IV.

Series B, $\perp$ type. The bands range from 8.5μ to 11.3μ . They are shown in Fig. 6 and the frequencies of the Q branches as observed are given in Table II.

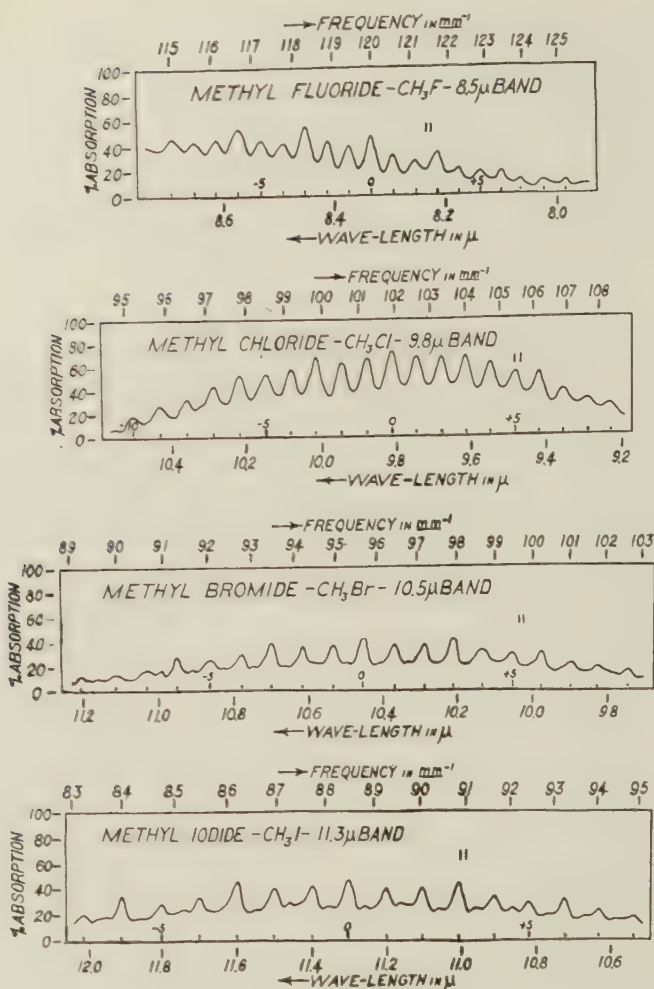


Fig. 6. The bands of series B.

TABLE II. The bands of series B, $\perp$ type.

Line No.	Observed frequencies, cm^{-1} .				Line No.	Observed frequencies, cm^{-1} .			
	CH_3F	CH_3Cl	CH_3Br	CH_3I		CH_3F	CH_3Cl	CH_3Br	CH_3I
-10		952.6			0	1200.0	1019.9	956.9	885.1
-9	1150.6	958.8	892.3		1	1206.0	1026.7	964.6	892.8
-8	1155.6	965.7	899.8		2	1211.6	1033.6	972.0	900.7
-7	1160.9	972.4	906.5	832.5	3	1217.0	1040.6	979.3	908.6
-6	1166.4	978.9	913.3	840.0	4	1222.8	1047.9	986.8	916.4
-5	1172.2	985.6	920.7	847.6	5	1228.4	1055.3	994.9	924.4
-4	1177.6	992.3	927.8	854.9	6	1234.2	1062.1	1002.5	932.6
-3	1183.1	999.0	934.8	862.4	7	1240.0	1069.5	1010.5	940.6
-2	1188.7	1006.0	942.3	869.7	8	1246.1	1076.7	1018.1	949.0
-1	1194.3	1012.9	949.5	877.5	9	1252.5	1083.8	1026.5	

In the curve for CH_3F it will be noted that the background of absorption rises continuously in the direction of greater wave-length. This band was observed with the gas in the cell at a pressure of 72.1 cm; it is thus much fainter than the neighboring band of series *A* at 9.55μ which was observed at a pressure of 4.0 cm. By raising the pressure from 4.0 cm to 72.1 cm the effective width of the band at 9.55μ of course increases very materially. By extending the measurements with the gas at a pressure of 72.1 cm beyond the limits of the curve represented for the 8.5μ band it was definitely established that the rising background was due to overlapping with the 9.55μ band which was broadened and intensified by the increased gas pressure. If it were not for this overlapping the maximum of absorption attained in the 8.5μ band would probably have been about 45 percent instead of about 55 percent as represented.

The band for CH_3Cl was measured at a pressure of 74.0 cm. It shows a percent absorption much greater than that of the band for CH_3F and hence the conclusion may be drawn that it is more intense than the latter, although less intense than the band for CH_3Br which was measured at 22.3 cm pressure. The band for CH_3I was measured at 21.8 cm pressure and appears to be the most intense band of the series. Slit-widths used in this region ranged between 100A and 200A.

In all of these bands, every third line is more intense than the others. Between the lines in the band for CH_3I and less pronouncedly in the band for CH_3Br , there appear faint lines. Repeated measurements of these intervals between the principal lines showed these faint lines to be real.

The positions of the principal lines converge, in the direction of *lower* frequencies. Expressed in waves per cm the positions can be represented by the following equations:

$$\begin{array}{ll} \text{for } \text{CH}_3\text{F} & \nu = 1200.10 + 5.650 n + .015 n^2 \\ \text{" } \text{CH}_3\text{Cl} & \nu = 1019.70 + 6.945 n + .022 n^2 \\ \text{" } \text{CH}_3\text{Br} & \nu = 957.00 + 7.420 n + .030 n^2 \\ \text{" } \text{CH}_3\text{I} & \nu = 885.15 + 7.700 n + .032 n^2 \end{array}$$

Since the coefficients of the quadratic terms are large, the perturbations are large for this type of vibration, also. It will be noted further that the coefficients of the quadratic terms become larger with increased atomic weight of the atom substituted in methane, which indicates that perturbations are somewhat larger in the cases of heavier atoms.

Series C, || type, and D, $\perp$ type. The two series of bands, which lie in the region of 7μ , are shown in Fig. 7. The bands of series *C* have unresolved *P*, *Q*, and *R* branches. In the three lower curves they lie on the left of the figure, and may be readily identified. In the upper curve, for CH_3F , the bands of series *C* and *D* are superposed. The bands of series *D* on the right, consist of a succession of *Q* branches. The frequencies of these are given in Table III. There are falsifications introduced into the measurements for this series of bands due to the fact that the water vapor of the atmosphere absorbs strongly in the region in which the bands lie. These falsifications are produced in three ways.

First, the available energy at certain settings of the grating is extremely small, causing the errors of observation to rise correspondingly. Second, the slit passes a range of wave-length which is somewhat greater than the width

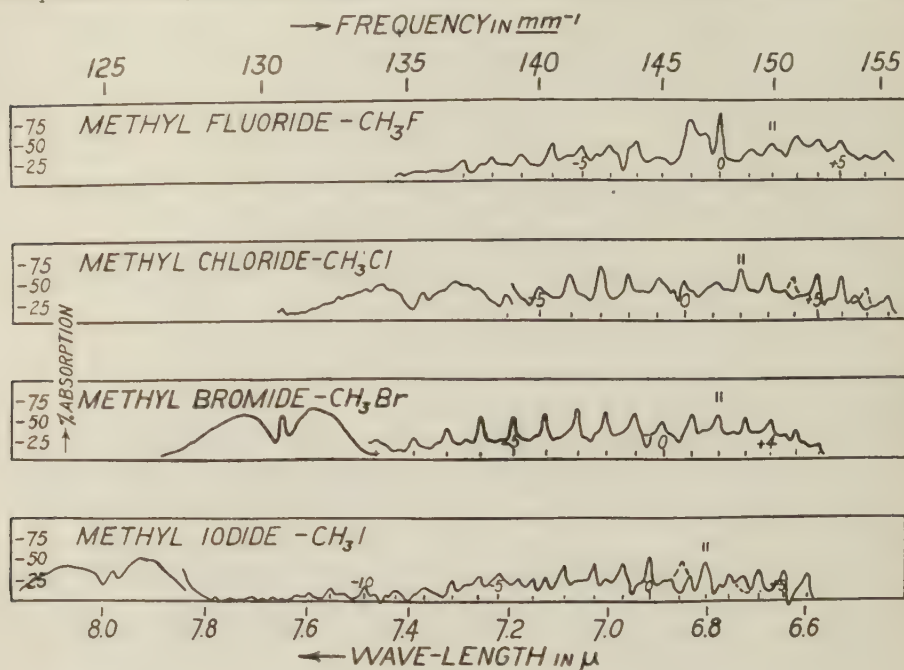


Fig. 7. The bands of series C (left) and series D (right).

of a line in either the water vapor or the methyl halide spectrum. If a line in each of these spectra happens to come at just the same wave-length, no great decrease in energy transmitted by the slit is noted although the line in the

TABLE III. The bands of series D, $\perp$ type.

Line No.	Observed frequencies, cm^{-1} .				Line No.	Observed frequencies, cm^{-1} .			
	CH_3F	CH_3Cl	CH_3Br	CH_3I		CH_3F	CH_3Cl	CH_3Br	CH_3I
-11				1323.7	-1	1463.8	1447.5	1438.7	1434.8
-10				1335.6	0	1475.7	1459.6	1450.5	1445.5
-9	1371.6		1339.0	1346.7	1	1487.9	1471.9	1463.0	—
-8	1381.7		1352.4	1356.9	2	1499.0	1484.3	1474.7	1470.1
-7	1392.7		1364.7	1367.6	3	1510.5	1496.7	1486.7	1480.5
-6	1404.8	1387.0	1377.5	1378.2	4	1521.1	—	1498.2	1494.0
-5	1416.9	1399.5	1390.0	1385.5	5	1531.6	1519.8	1509.5	1505.6
-4	1428.2	1412.4	1402.3	1398.3	6	1542.0	1531.6	1520.3	1515.9
-3	1439.5	1424.3	1415.3	1410.6	7	1551.0	—		
-2	1451.5	1435.9	1426.7	1422.9	8		1554.0		

methyl halide spectrum at this wave-length may be quite intense. Third, there is an effect due to the very steep slopes in the energy curve which are present in a region of water vapor absorption, considered in conjunction with

minute alterations of the beam which occur when the absorption cell is introduced. The explanation of this effect is involved, and will not be given in detail.

Slit widths corresponding to about 70A were used, and readings were taken at an interval of about 75A. Measurements were also made on the $\parallel$ band for the chloride using a slit width of 35A and taking a large number of readings at each point. These measurements showed a suggestion of fine structure, but not a sufficient one to justify continuing the measurements with this slit width. The pressures of gas in the cell are given in Table V. For the band of Series *D* of methyl iodide it was necessary to use a special cell for reasons which will be given presently.

The positions of the *Q*-branches in series *D* are not as accurately given as those of series *B*. The observed data for CH_3F and CH_3I fall too irregularly to allow conclusions to be drawn in regard to convergence. The data for CH_3Cl and CH_3Br however indicate a convergence of the lines in the direction of *higher* frequencies. But the irregularities are too great to permit giving expressions for the frequencies in which the quadratic terms would have significance. The linear terms (average intervals between the lines) are given in Table VIII.

TABLE IV. *Maxima of the envelopes of the branches, $\parallel$ bands.*

	Observed frequencies			Doublet Spacing $\nu_P - \nu_R$
	<i>P</i> -branch	<i>Q</i> -branch	<i>R</i> -branch	
Series <i>A</i> CH_3F CH_3Cl	1023 cm^{-1} 712	1048.5 cm^{-1} 732.3	1066 cm^{-1} 747	43 cm^{-1} 35
Series <i>C</i> CH_3F CH_3Cl CH_3Br CH_3I	— 1341 1293 1240	1475.7 1355.3 1305.5 1251.8	— 1369 1318 1263	— 28 25 23
Series <i>E</i> CH_3F CH_3Cl CH_3Br CH_3I	2841 2868 2850 2851	2862.4 2879.6 — —	2985 2891 2873 2872	44 23 23 21
Series <i>F</i> CH_3F CH_3Cl CH_3Br CH_3I	— 2953 2961 2960	2965.3 2967.0 — (2970.6)	— 2981 2984 2981	— 28 23 21

Series E and F, $\parallel$ type, and G, $\perp$ type. The three series of bands, lying in the 3μ region are shown in Fig. 8. The bands of series *E* and *F* have unresolved *P*, *Q*, and *R* branches. The *Q* branches are strong only in the case of the fluoride. For the other three compounds they are weak, and in some cases are not recorded. The frequencies of the maxima of the envelopes of the branches are given in Table IV. The frequencies of the succession of *Q*

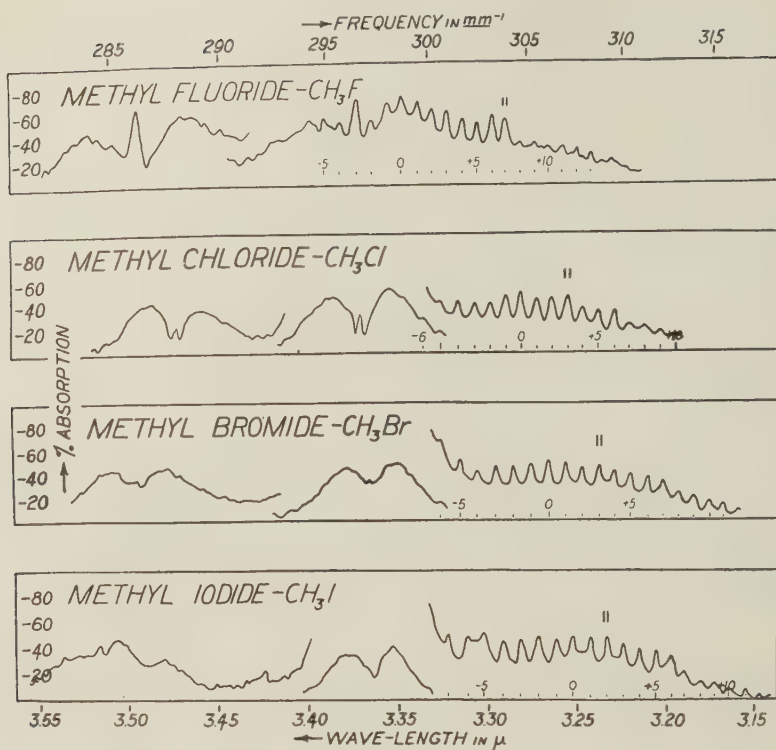


Fig. 8. The bands of series E (left), F (center), and G (right).

TABLE V. Pressures of gas in absorption cell.

	Series C	Series D
CH ₃ F	31.4 cm	31.4 cm
CH ₃ Cl	11.3	30.8
CH ₃ Br	8.3	28.3
CH ₃ I	11.9	40. (10 cm cell)

TABLE VI. The bands of series G, $\perp$ type.

Line No.	Observed frequencies, cm ⁻¹ .				Line No.	Observed frequencies, cm ⁻¹ .			
	CH ₃ F	CH ₃ Cl	CH ₃ Br	CH ₃ I		CH ₃ F	CH ₃ Cl	CH ₃ Br	CH ₃ I
-7		2989.0		3009.4	3	3009.6	3071.7	3088.2	3100.9
-6	2942.6	2998.2	3005.5	3019.3	4	3017.7	3079.6	3096.6	3109.9
-5	2949.4	3006.5	3015.3	3027.5	5	3024.9	3087.8	3104.5	3118.8
-4	2957.2	3015.4	3023.8	3037.5	6	3032.5	3096.7	3113.9	3127.3
-3	2965.3	3024.2	3034.3	3046.8	7	3039.2	3104.6	3122.3	3134.5
-2	2972.3	3031.7	3042.8	3056.2	8	3047.3	3112.5	3131.0	3143.8
-1	2980.2	3039.8	3052.3	3065.4	9	3054.5	3121.0	3138.6	3151.4
0	2987.2	3047.2	3061.5	3074.2	10	3061.3	3129.2	3147.2	3159.2
1	2995.0	3055.5	3070.2	3083.6	11	3068.8		3155.2	3168.9
2	3002.2	3063.2	3079.3	3092.4	12	3076.5		3163.8	3176.8
					13	3083.8			

branches in the bands of series *G* are given in Table VI. In the case of the fluoride the bands of series *F* and *G* overlap, as do the aforementioned bands of series *C* and *D* for this compound. The greater intensity of every third line is again noticeable in series *G*, but it is less evident than in series *B*, Fig. 6. The failure to record the intensification of every third line in series *D*, Fig. 7, may well be due to the falsification introduced by the water vapor of the atmosphere.

Slit widths of from 30A to 43A were used and readings were taken at an interval of 17A. The pressures of gas in the cell are given in Table VII. The bands for the iodide in series *D*, *E*, and *G* are weak and it was necessary to use

TABLE VII. *Pressures of gas in absorption cell.*

	Series <i>E</i>	Series <i>F</i>	Series <i>G</i>
CH ₃ F	14.4 cm	6.4 cm	6.4 cm
CH ₃ Cl	19.5	5.0	17.4
CH ₃ Br	23.9	5.3	50.5
CH ₃ I	40. (10 cm cell)	10.0	40. (20.8 cm cell)

a cell of greater length than the one of 6 cm which has otherwise been used throughout. A cell of variable length with mica windows and carefully selected compensating windows was available. All of the windows made an angle of 30° with the beam to avoid interference effects which occur when the thin windows are used perpendicularly to the beam.¹³ For the band in series *E* the cell was adjusted to a length of 10 cm, and it was allowed to fill with the saturated vapor of the iodide by letting it stand for a day with a small flask of liquid iodide in the cell at 25°C. The vapor pressure of methyl iodide at this temperature is 40 cm. For the band in series *G*, the cell was adjusted to a length of 20.8 cm and the same procedure was followed. The band of series *E* for the iodide does not present a clear structure. Because of a fear that mica interference effects might still be present, measurement of this band was repeated using a cell with rock salt windows, having a length of 10 cm. Practically the same curve was obtained.

The *Q* branches, in series *G*, converge in position in the direction of *higher* frequencies. Moreover, the convergence increases in passing from the fluoride to the chloride, the bromide, and the iodide, indicating again larger perturbations in the cases of heavier atoms. The observed data when plotted do not, however, have sufficient regularity to justify giving expressions for the frequencies involving quadratic terms. The average intervals between the lines are given in Table VIII.

In the bands of series *E* and *F* the intensities of the *Q* branches diminish in passing through each series from the fluoride to the iodide, or from the lighter to the heavier halide, a circumstance which may be understood by applying the intensity expression found by Dennison, Reiche and Kronig.¹

¹³ C. F. Meyer and D. W. Bronk, *Astrophys. Journ.* 59, 252 (1924).

The bands of series *E* for the chloride, bromide, and iodide progress quite regularly toward the wave-length, 3.31μ , found by Cooley¹¹ for the band of methane in this region, while the band of the fluoride is somewhat out of position. It was thought that perhaps this band was a member of still another series, fainter than these three, whose bands lay at longer wave-lengths for the compounds with higher atomic weight of the substituted atom. Explorations to 4.5μ with the cell filled to atmospheric pressure with CH_3Cl showed no absorption, so it was concluded that this band of CH_3F must be a quite irregularly placed member of series *E*.

COMPARISON BETWEEN SERIES

The frequency intervals between the points of maximum absorption of the *P* and *R* branches in the bands of the $\parallel$ type are on the whole the same for the bands of any compound in different series. This frequency interval is commonly referred to as the doublet separation of the band. For the fluoride, it has been possible to determine the doublet separation for only two bands because of the overlapping of the remaining two bands of the $\parallel$ type with those of the $\perp$ type. The two doublet separations which have been determined agree to within the experimental accuracy. The four doublet separations recorded for the chloride do not agree, but range in value from 35 cm^{-1} for the band of series *A*, to 23 cm^{-1} for the band of series *E*, exhibiting a divergence which may or may not be real. Those for the bromide and iodide agree as nearly as they can be determined. Table IV gives the doublet separations for all the bands which could be measured.

The simple theory predicts that the frequency interval between the *Q* branches in the bands of the $\perp$ type for each compound will be the same for all the bands of this type for the compound. It has been found, however, that this is not the case. Table VIII gives the average interval between the lines

TABLE VIII. *Average frequency intervals between lines.*

Methane, CH_4	5.4 cm^{-1} (region of 7.7μ)		9.8 cm^{-1} (region of 3.3μ)
Methyl halides	Series <i>B</i>	Series <i>D</i>	Series <i>G</i>
CH_3F	5.65 cm^{-1}	11.5 cm^{-1}	7.5 cm^{-1}
CH_3Cl	6.95	12.0	8.2
CH_3Br	7.42	11.9	9.0
CH_3I	7.70	11.8	9.0

in the bands of all the regions observed. The separations of the lines for the bands in series *D* are seen to be nearly twice those of the bands of series *B* for corresponding compounds, while the separations in series *G* have intermediate values.

It appears that the explanation of this phenomenon must come from a deeper understanding of the mechanism of this type of vibration and its interactions with rotation. It is clear, however, from the general form of the spectrum that the methyl halide molecule must be of the symmetrical type,

and in fact, recourse to an unsymmetrical model having three different moments of inertia would in no way serve to explain either the general features of the spectrum or the structure of the $\perp$ bands.

In conclusion the authors wish to acknowledge their indebtedness to Professor D. M. Dennison, who has given liberally of his time and energy in studying and discussing the interpretation of the experimental results.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MICHIGAN,
AUGUST, 1928.

Note added to proof, Oct. 27th: Professor Firestone has recently taken some Raman spectrograms of methyl bromide and methyl iodide, in liquid form, from which it was hoped to determine the positions of the bands of Series *A* for the two compounds. These bands have eluded detection by direct infra-red methods, as above mentioned. The first photographs, while showing Raman lines, do not permit definite conclusions to be drawn. It is hoped that an announcement of the results may shortly be made in the form of a note in this journal.

